SEMI-ANNUAL STATUS REPORT

NASA GRANT NGR-12-001-012

to the

GEOCHEMISTRY DIVISION

HAWAII INSTITUTE OF GEOPHYSICS

UNIVERSITY OF HAWAII

titled

"Search for Biological Precursor Molecules

in Volcanic Volatile Systems"

Prepared by

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February 1, 1965 - August 1, 1965

1. Subject: Semi-annual Status Report

NASA Grant NGR-12-001-012

2. Title: "Search for Biological Precursor Molecules in Volcanic Volatile Systems."

3. Abstract.

The research consists of the following two parts - (1) an investigation of the natural volcanic gaseous system for its elemental and molecular composition, with particular emphasis on compounds of biological importance which might be present in trace quantities. (2) A laboratory investigation of the equilibrium molecular and free radical components to be found in gaseous systems which contain the major elements (O, H, C, S, N) in the proportions present in volcanic gas. This last is pertinent since we have found from work on Hawaiian volcanoes that the gases are a homogenous system in thermodynamic equilibrium. Comparison of the components found in the experimental situation (and expected from theoretical calculations, where possible) with those found in nature, are being made; again with emphasis on substances which might relate to life processes.

4. General Statement.

This grant was activated on February 1, 1965, but due to certain delays it did not become operative for experimental work until mid-March. Much of the effort has been devoted to equipment construction and sample collection, but a few very tentative preliminary results have been obtained.

5. Volcanic Gas Collection Conditions During Feb. 1 - July 31, 1965.

(a) Kilauea Eruption. Makaopuhi, 1965.

We were fortunate early in March, 1965, to have had a flank eruption of Kilauea volcano on Hawaii. This occurred along a rift extending from a prehistoric pit crater (Makaopuhi) to inaccessible regions in the rain forest. It persisted for about two weeks, and in its later phases lava fountaining was limited to a rift on the wall of the pit crater which was filled with a molten lava lake to a depth of approximately two hundred feet. Exact details will be published by the U. S. Geological Survey.

During two periods of the eruption, with the help of the staff of the Hawaii Volcano Observatory, we were able to get a group to the edge of the lava lake under extremely difficult and unpleasant conditions. Gas samples were taken directly from the surface of the lava lake and from the momentarily persistent holes left after the removal of ceramic tubes which were used to collect molten lava samples.

(b) Drill Hole Sampling.

The staff of the Hawaii Volcano Observatory, U. S. Geological Survey, has a program of drilling into crusted-over lava lakes which have been the by-products of recent eruptions at Kilauea (Kilauea-Iki, Alae, and now Makaopuhi Crater). These have been used for a variety of researches, and we have been cooperating in work on the gases from these

drill holes Drilling has been undertaken through the thin crust of the new lake at Makaopuhi, and gas samples have been taken both at the bottom and at intermediate levels in these holes.

(c) Solfataric Areas.

Gas collections by adsorption tube techniques have been made as frequently as possible at the old fumarole at Sulfur Bank on the rim of Kilauea Caldera, in order to follow any changes of gas composition with the erupting phase of the volcano. A new solfataric area on the south rim of the caldera, pointed out by Dr. Howard Powers of the Observatory, also has been sampled.

(d) Gases in Rock Vesicles and Inclusions.

By the use of enclosed crushers of various designs, gases have been released from lava and pumice within a few days of eruption, and analyzed by means of gas chromatography. Also the gases present in inclusions from nodules of the 1801 eruption of Hualalei volcano were examined by this same method.

6. Equipment for Collection of Volcanic Gases.

(a) Gas Adsorption Tubes.

Gas adsorption tubes utilizing the chromatographic principle, which have been described previously [J. Geophys. Res. 68 539 (1963)] continue to be used for surface collections. Some slight but important modifications have been made in the design of these tubes, but the basic principle and method of use remains the same.

(b) Drill Hole Collection Tubes.

In order to withstand the high temperatures inside drill holes at collection points (to 1200°C), adsorption tubes were enclosed in vitreous silica tubes with the intermediate space filled with a diatomaceous earth thermal insulating material. The break-off tip of the tubes could be broken by impact at the bottom, or by a "traveler" or pull-wire at intermediate positions in the drill hole.

7. Analytical Methods.

(a) Aqueous Condensate Analysis for Minor Constituents.

Condensate water from collection tubes and fumaroles was extracted into organic solvents, and separate portions were evaporated to dryness after making neutral, acidic and basic. The derived materials pelletized with KBr were analyzed using infrared adsorption.

(b) Gas Chromatographic Analysis.

The main method used for gas analysis was the important technique of gas chromatography. The particular combination of major component gases found in volcanic effluvia is difficult to analyze accurately by any method, and we are continually changing our equipment in order to simplify and improve this technique. The trend is to use a single detector with multi-column switching to accommodate the variety of components to be analyzed. In order to detect carbon containing molecules which might be present in very minor amounts in the gases, a borrowed

flame ionization detector system has been installed, and currently is just being tested on volcanic samples.

(c) Mass Spectrometry.

An analytical mass spectrometer has been constructed, as was outlined in the proposal for this research. This will be used dynamically (1) to analyze for minor components in volcanic gas fractions, and (2) to examine gas from a reactor producing "volcanic gases" in the laboratory to search for unexpected components of biological importance.

The unit has been assembled, and currently the vacuum components of the spectrometer and sample systems are being vacuum tested and baked to achieve conditions needed for operation.

(d) Computer Programming.

The assumption has been made that prebiologic molecules in volcanic volatile systems would partake of the equilibrium characteristics which have been shown to be attained for the major components. This being the case, the equilibrium concentration of these substances can be calculated for a system with the basic atomic composition (H, O, C, S, N) of volcanic gas. A computer is necessary for such calculations, and we have extended previous programs to include additional atoms (N) necessary in biological systems, and to make them satisfactory for use in our present computer (IBM 7040).

Currently programs are being "debugged."

(e) Infrared Spectrophotometry.

Infrared methods have been used in examining volcanic condensates (KBr pelleting), and gases (10 meter gas cell) for molecules and systems of possible prebiological importance.

8. Results.

(a) Gas Chromatographic Analysis of Drill Hole and Fumarolic Samples.

The following carbon containing molecules have been found to date as components of these samples:

Major - CO_2

Minor - CO, CH_4 (sporadic and rare).

Using the flame ionization detector, which is sensitive only to carbon containing molecules (other than CO_2 and CO), no notable identifications have been made in the two samples tested with this detector to date, but some anomalous peaks have been noted which will bear further investigation.

(b) Gas Chromatographic Analysis of Fluid Inclusions in Deep-Seated Rocks, and in Newly Erupted Pumice and Lava.

Only gases found to date: CO_2, H_2O, N_2.

(c) Infrared Spectrophotometric Investigation of Fumarolic Violatiles.

The ammonium ion has been found in condensate from one of our fumaroles, although the associated anion has not been identified with certainty as yet. This is the first instance

where this has been reported, and will require careful further checking. This ion would be most important in any prebiologic system.

9. Conclusions (highly tentative).

The presence of quantities of ammonia and carbon dioxide in these gases, and the rarity of methane, would seem to lend sustenance to a Wohler synthesis of urea as a pathway to more complex organic molecules in a primitive aqueous environment derived from basaltic volatiles. Indeed a route from urea to the important high energy phosphate, carbamyl phosphate, has recently been suggested by Miller and Parrish [Nature 204 1248 (1964)].

10. Changes of Direction of Research or Procedures from that Outlined in Proposal.

No changes in the basic direction of the research has occurred or is anticipated for the near future.

With regards to personnel, it was found impossible to take on a Graduate Student Research Assistant, as indicated in the Proposal, because of the particular time of the year at which the grant was activated. To compensate in this need for manpower, additional student help have been employed, especially during the summer period.

Respectfully submitted,

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